

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements relating to Synthetic Rubbers

I, PERCY FREDERICK COMBE SOWTER, a British subject, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the manufacture of synthetic rubbers.

In the production of synthetic rubbers by co-polymerisation of a di-olefine, e.g. butadiene, with an unsaturated nitrile, e.g. acrylonitrile or methacrylonitrile, it has been found that the products have a persistent unpleasant smell. It is an object of the present invention to remove this disadvantage of such products.

It was thought possible that the constituent or constituents responsible for the smell might be extracted from the vulcanised synthetic rubber by steeping this in a suitably chosen liquid. Numerous liquids were investigated from this point of view. It was found that liquid petroleum fractions were without substantial effect on the smell. Aromatic hydrocarbons, e.g. benzene, toluene and the xylenes, besides producing great swelling of the synthetic rubber did not remove the smell, apparently owing to retention in the highly swollen material of a solution of the constituent responsible for the smell, in the aromatic hydrocarbon. Lower aliphatic ethers, e.g. dimethyl ether, methyl ethyl ether and diethyl ether, and lower aliphatic ketones, e.g. acetone and methyl ethyl ketone, though capable of substantially removing the smell, at the same time swelled the material to an undesirable degree.

I have now found that the smell can be removed from the vulcanised synthetic rubber without substantial swelling, by extraction with a lower alcohol, e.g. methanol, ethanol or isopropanol. The extraction can be carried out by steeping the synthetic rubber in the alcohol for 12

to 24 hours at ordinary temperatures, or by a shorter treatment at a higher temperature, e.g. 1 hour at the boiling point of the alcohol.

One method of carrying out the invention is as follows:—A synthetic rubber is made by co-polymerising butadiene-1:3 and methacrylonitrile in the proportions of 3:1 by weight in an aqueous emulsion buffered with sodium phosphate, using sodium secondary octadecyl sulphate as emulsifying agent, starch as protective colloid, *n*-octanol as froth inhibitor, carbon tetrachloride as regulator and benzoyl peroxide as catalyst. The synthetic rubber, obtained in the form of a latex, is coagulated after the addition of about 1% (based on the weight of synthetic rubber contained in the latex) of N.N'-di-beta-naphthyl-*p*-phenylene diamine, by the action of an aqueous solution of sulphuric acid and sodium chloride. The acid is neutralised and the coagulum is compounded with 1% of diphenyl guanidine, mercaptobenzthiazole or benzthiazyl disulphide, 5% of zinc oxide, 45% of carbon black and 2 to 3% of sulphur, these percentages being based on the weight of the synthetic rubber. The synthetic rubber mix is calendered and vulcanised.

The vulcanised synthetic rubber sheet has a strong unpleasant smell. It is steeped for 18 hours in industrial alcohol (ethanol denatured with 5% methanol and 5% acetone) at 20° C. During this treatment the material is swollen to the extent of 6% expressed as increase in weight. The material is removed from the alcohol bath, and dried by evaporation. It is found to have lost about 4% by weight and to be substantially odourless. Under the same conditions, liquids typical of the other classes referred to above gave the following results:

	Liquid	Increase in weight (%)	Loss of weight (%) after drying	Smell
5	Petroleum Ether -	16	1	Unchanged
	Benzene - - -	230	5	Slightly reduced
	Diethyl Ether - -	41	12	Substantially removed
	Acetone - - -	90	12	Substantially removed
10	Treatment with the alcohol specified, at the boil for 1 hour, removed the smell, producing a swelling of 15% and a loss in weight of 7%.			
15	Other co-polymers of di-olefines with unsaturated nitriles can be de-odourised as described above, e.g. co-polymers of butadiene with acrylonitrile or of isoprene, piperylene or 2:3-dimethyl butadiene with acrylonitrile or methacrylonitrile.			
20	I have also found that the method described above is suitable for removing from co-polymers of di-olefines with styrene or a substituted styrene, an objectionable smell which is sometimes found, apparently owing to the inclusion in the product of small quantities of constituents of the polymerisation emulsion. The following is an example of such a treatment:—			
30	A synthetic rubber is made by co-polymerising butadiene-1:3 and styrene in the proportions of 3:1 by weight in an aqueous emulsion of the kind described above in connection with the co-polymerisation of butadiene and acrylonitrile.			
35	The synthetic rubber so obtained has a smell less pronounced than that of co-polymers of acrylonitrile or methacrylonitrile, but which for some use of the synthetic rubber might be objectionable. The			
40				
	synthetic rubber is steeped first for 18 hours at 20° C. in industrial alcohol, removed dried and steeped again in fresh industrial alcohol at the same temperature for 48 hours. After the first extraction the smell is much fainter, the material has imbibed 7% of its weight of the alcohol and after drying has lost 3% of its weight. After the second extraction the smell is substantially absent, the imbibition is 8% and the loss of weight 2%. Similar results can be obtained more quickly at higher temperatures, e.g. by two successive extractions, each for 1 hour, with the alcohol at the boil.			
	It will be appreciated that the treatment of the synthetic rubber can be applied before or after vulcanisation.			
	After the de-odourising treatment of the invention a pleasant smell may be imparted to the synthetic rubber if desired by the application of a perfume in solution in a liquid which does not unduly swell the synthetic rubber, e.g. methanol, ethanol or isopropanol.			
	Dated this 2nd day of July, 1945.			
	STEPHENS & ALLEN, Chartered Patent Agents, Wykeham House, Gordon Avenue, Stanmore, Middlesex.			

COMPLETE SPECIFICATION

Improvements relating to Synthetic Rubbers

I, PERCY FREDERICK COMBE SOWTER, a British subject, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of synthetic products, and in particular of synthetic rubbers.

In the production of synthetic rubbers by co-polymerisation of a di-olefine, e.g. butadiene, with an unsaturated nitrile, e.g. acrylonitrile or methacrylonitrile, it has been found that the products have a

persistent unpleasant smell. It is an object of the present invention to remove this disadvantage of such products.

It was thought possible that the constituent or constituents responsible for the smell might be extracted from the vulcanised synthetic rubber by steeping this in a suitably chosen liquid. Numerous liquids were investigated from this point of view. It was found that liquid petroleum fractions were without substantial effect on the smell. Aromatic hydrocarbons, e.g. benzene, toluene and the xylenes, besides producing great swelling of the synthetic rubber did not remove the smell, apparently owing to retention in the

highly swollen material of a solution of the constituent responsible for the smell, in the aromatic hydrocarbon. Lower aliphatic ethers, e.g. dimethyl ether, methyl ethyl ether and diethyl ether, and lower aliphatic ketones, e.g. acetone and methyl ethyl ketone, though capable of substantially removing the smell, at the same time swelled the material to an undesirable degree.

I have now found that the smell can be removed from the vulcanised synthetic rubber without substantial swelling, by extraction with a saturated mono-hydric-alcohol containing not more than 4 carbon atoms, e.g. methanol, ethanol or isopropanol. The extraction can be carried out by steeping the synthetic rubber in the alcohol for 12 to 24 hours at ordinary temperatures, or by a shorter treatment at a higher temperature, e.g. 1 hour at the boiling point of the alcohol. As an alternative the treatment can be applied to the synthetic rubber in the unvulcanised state.

Other co-polymers of diolefines with unsaturated nitriles can be de-odourised as described above, e.g. co-polymers of butadiene with acrylonitrile or of isoprene, piperylene or 2:3-dimethyl butadiene with acrylonitrile or methacrylonitrile.

The present invention therefore comprises a process for treating a synthetic rubber which is a co-polymer of a diene hydrocarbon and a nitrile of the formula $\text{CH}_2=\text{C}(\text{R})\text{CN}$, where R is hydrogen or alkyl, and which has an unpleasant smell, which comprises extracting malodourous contaminants from said synthetic rubber by treatment with a saturated mono-hydric-alcohol containing not more than 4 carbon atoms.

The following Examples illustrate the invention:—

EXAMPLE 1.

A synthetic rubber is made by co-polymerising butadiene-1:3 and methacrylonitrile in the proportions of 3:1 by weight in an aqueous emulsion buffered with sodium phosphate, using sodium secondary octadecyl sulphate as emulsifying agent, carbon tetrachloride as regulator and benzoyl peroxide as catalyst. The synthetic rubber, obtained in the form of a latex, is coagulated after the addition of about 1% (based on the weight of synthetic rubber contained in the latex) of N.N'-di-beta-naphthyl-p-phenylene diamine, by the action of an aqueous solution of sulphuric acid and sodium chloride. The acid is neutralised and the coagulum is compounded with 1% of diphenyl guanidine, mercaptobenzthiazole or benzthiazyl disulphide, 5% of zinc oxide, 45% of carbon black and 2 to 3% of sulphur, these percentages being based on the weight of the synthetic rubber. The synthetic rubber mix is calendered and vulcanised.

The vulcanised synthetic rubber sheet has a strong unpleasant smell. It is steeped for 18 hours in industrial alcohol (ethanol denatured with 5% methanol and 5% acetone) at 20° C. During this treatment the material is swollen to an extent indicated by an increase in weight of 6%. The material is removed from the alcohol bath, and dried at about 30° C. by evaporation. It is then found to have lost about 4% by weight and to be substantially odourless. Under the same conditions, liquids typical of the other classes referred to above gave the following results:—

85	Liquid	Increase in weight (%)	Loss of weight (%) after drying	Smell
	Petroleum Ether	16	1	Unchanged
	Benzene	230	5	Slightly reduced
	Diethyl Ether	41	12	Substantially removed
90	Acetone	90	12	Substantially removed

Treatment with the alcohol specified, at the boil for 1 hour, removed the smell, producing a swelling of 15% and a loss in weight of 7%.

EXAMPLE 2.

The process is carried out as in Example 1 except that the polymerisation is carried out in an alkaline aqueous medium containing sodium linoleate as emulsifying

agent, potassium persulphate as catalyst and bis-isopropyl xanthogen as modifier.

EXAMPLE 3.

The process is carried out as in Example 2 but using sodium oleate as emulsifying agent and dodecyl mercaptan as modifier.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be

performed, I declare that what I claim is:—

1. Process for treating a synthetic rubber which is a co-polymer of a diene hydrocarbon and a nitrile of the formula $\text{CH}_2=\text{C}(\text{R})\text{CN}$, where R is hydrogen or alkyl, and which has an unpleasant smell, which comprises extracting malodourous contaminants from said synthetic rubber by treatment with a saturated monohydric alcohol containing not more than 4 carbon atoms.

2. Process according to Claim 1, wherein the diene hydrocarbon is butadiene and the nitrile is acrylonitrile or methacrylonitrile.

3. Process according to Claim 1 or 2, wherein the synthetic rubber is treated in the unvulcanised condition.

4. Process according to Claim 1 or 2,

wherein the synthetic rubber is treated in the vulcanised condition.

5. Process according to any of Claims 1 to 4, wherein the alcohol is ethanol.

6. Process for treating a synthetic rubber which is a co-polymer of a diene hydrocarbon and a nitrile of the formula $\text{CH}_2=\text{C}(\text{R})\text{CN}$, where R is hydrogen or alkyl, and which has an unpleasant smell, which comprises extracting malodourous contaminants from said synthetic rubber by treatment with a saturated monohydric alcohol containing not more than 4 carbon atoms, substantially as hereinbefore described.

Dated this 21st day of May, 1946.

STEPHENS & ALLEN,
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